April 25, 2003

TO: Drinking Water Compliance Laboratories

FROM: California Department of Health Services
                2151 Berkeley Way
                Berkeley, CA 94704

SUBJ: Draft QC Protocol for Synthetic Organic Chemical (SOCs) Analyses

The purpose of this memo is to request your feedback on the Department of Health Services (Department)'s draft QC Protocol for Synthetic Organic Chemical Analyses, which is attached.

Background   As you may recall, in 1999, the California Department of Health Services (DHS) established a workgroup [Reporting Level Workgroup (RLWG)] of representatives from a number of commercial laboratories throughout the state and staff from the Sanitation and Radiation Laboratory (SRL) and the Division of Drinking Water and Environmental Management. The objective was to develop a procedure for setting inorganic chemical (IOC) reporting levels [officially known as Detection Levels for Purposes of Reporting (DLRs)] for regulated drinking water contaminants. A procedure was developed with the help of data from an interlaboratory study of 55 volunteer commercial laboratories; the outcome was scientific verification of some existing DLRs and the derivation of several new DLRs for various metal IOCs by a process based on study data.

The RLWG concluded from its study that some laboratories would have difficulties in achieving adequate data quality at or near the DLR with certain metal IOCs and methods, even though those methods are presently approved by EPA. Since the RLWG preferred to not eliminate any of the EPA-approved methods as options, it decided to develop a QC protocol to assist laboratories in determining their performance at or near the DLR and improve the quality of analytical data for metal IOCs. The recommended protocol has been posted on the DHS website to be used in addition to protocols prescribed by the EPA-approved methods. There should be little or no incremental cost impact.

Draft protocol development Such a protocol is also needed to address synthetic organic chemical (SOC) compliance sample analyses. However, issues arise in the analysis of SOC samples that do not for inorganics. For that reason and the fact that there is no interlaboratory study data set available for the SOCs, SRL has approached the need to improve the quality of SOC data in a different way.   As for the metals, there are two aspects to improving the data. One aspect is to ascertain that the DLRs are actually achievable by most commercial laboratories within an acceptable range of precision and accuracy. The other aspect is to identify those

methods and analytes for which achieving the DLR can be difficult and provide a protocol for improving the precision and accuracy in those cases.

To assess the current SOC DLRs, SRL compiled the relevant available information for each regulated organic chemical: EPA approved methods, EPA MDLs, and state detection levels for purposes of reporting (DLRs), MCLs, and public health goals (PHGs). Next, to identify those methods for which difficulties in achieving adequate data quality at or near the DLR exist, SRL assessed reporting levels equivalent to 3 times the MDL for each method and chemical in terms of meeting the existing state DLR and in relationship to the current MCL and PHG, if established. Attached is a table with the information presented.

To improve the quality of the data for methods/chemicals presenting difficulties, SRL drafted the attached approach consisting of the components A and B.

Please review these materials and return any comments by June 2, 2003, to Kusum Perera at 2151 Berkeley Way, Berkeley, CA. 94704. Thank you in advance for your comments.

Sincerely,

Alexis M. Milea, M.S., P.E., Chief
Standards and Technology Unit
Division of Drinking Water
  and Environmental Management
Department of Health Services

Attachments:
SOCs Draft QC Protocol
SOCs MDL-DLR Table

QC Protocol for SOCs
Draft-April 16, 2003

The QC protocol has two components (A and B): Component A applies to all methods and analytes and is to be performed with every batch of samples to assure adequate data quality for analyte concentrations at or near the DLR. Component B applies to method/analyte combinations for which there is evidence that they may give marginal performance at or near the DLR. It is to be performed at least once annually to evaluate a laboratory's basic capability to reliably quantitate an analyte at the DLR level by a given method.

Component A – Check Standard:

After an instrument is calibrated for SOC analysis, a check standard containing the analyte(s) of interest at the DLR level(s) is analyzed as a QC sample. The acceptance criterion for the result is:

Measured concentration = Concentration of DLR check standard $\pm$ 60%.

Failure of this test may indicate a systematic problem with the way the calibration curve was constructed. Remedial action should be taken at this point. This may include the use of weighted linear regression, or limiting the concentration range of the calibration curve.

The check standard is analyzed again with every batch of 20 or fewer samples and at the end of an analytical sequence. The acceptance criterion for these subsequent measurements is the same as above.

The ability to pass this test consistently throughout an analytical sequence demonstrates that the analysis remains in control and that adequate data quality can be achieved at or near the DLR level.

In addition to the DLR check standard, a laboratory reagent blank is analyzed with each batch of 20 samples or less and at the end of an analytical sequence. The analyte concentration measured for this blank should be < 40% of the DLR concentration.

Component B – MDL and Fortified Concentration Tests:

Component B applies only to those methods and analytes for which EPA's published MDL does not meet the criterion of 3 x MDL_{EPA} = DLR. (Note: The selection of 3 x MDL is based on EPA's definition of a quantification limit, 3.18 x MDL. This definition is also similar to the ACS' quantification limit, 10 x s at zero concentration.) The laboratory should demonstrate that the actual MDL achieved in the laboratory meets the criterion before proceeding with the fortified concentration test. Failure to

meet the MDL criterion, indicates that the method has insufficient sensitivity for quantification at the DLR.

After meeting the MDL criterion, the laboratory prepares a solution fortified with the analyte(s) of interest at or below the DLR level. The test matrix is appropriately acidified reagent water. The test solution is analyzed seven times over the course of three non-consecutive days. The results are averaged and compared to the fortified value(s). The acceptance criteria for this test are:

> RSD = 30%
> Average result = Fortified concentration ±30%

This test should be performed at the same frequency as the MDL determinations required for a given analyte and method (i.e., at least once annually, when a new analyst begins work, or whenever a change in analytical performance caused by either a change in instrument hardware or operating conditions dictates a redetermination). In cases in which the MDL is close to the DLR, it may be possible to select the same test concentrations for the MDL determination and the DLR performance test and do the two tests simultaneously.

Rationale for Selection of Acceptance Criteria

The general data quality objectives for SOCs measurements by a single laboratory at the DLR include expectations that the precision is 30% (RSD) or better and that the accuracy is true value ± 30% or better.

In the Component A test, the accuracy acceptance criteria are set at ± 60%, since with a sample standard deviation of 0.3 x DLR, about 95% of all measurements should fall in the range DLR ± 60%.

In the Component B test, seven replicate measurements are performed at the DLR level. If the sample standard deviation s is 30% of the DLR, the mean of seven measurements should be in the range DLR ± t(s/sqrt(n)), where n = 7. The t-value for a two-tailed test with 6 degrees of freedom and a confidence level of 95% is 2.45. Thus, the term t(s/sqrt(n)) corresponds to 28% of the DLR. This value is rounded up to give an acceptance range of ± 30%.

If the result for the laboratory reagent blank exceeds 40% of the DLR level, it is unlikely that acceptable accuracy at the DLR concentration can be achieved.

Regulated SOCs for which One or More of the EPA Approved Methods Do Not Meet the Criterion: 3 x MDL = DLR

SOC	EPA Approved Method	Method Rev# (Yr)	EPA MDL (µg/L)	Does EPA Listed MDL Meet the Criterion: 3xMDL = DLR?	Title 22 DLR (µg/L)	Title 22 MCL (µg/L)	CA PHG (µg/L)	EPA MCLG (µg/L)
Atrazine	505	R2.1 (95)	2.4	No, 3 x MDL=7.2	1	3	0.15	3
	507	R2.1 (95)	0.015	Yes				
	508.1	R2.0 (95)	0.003	Yes				
	525.2	R2.0 (95)	0.076	Yes				
	551.1	R1.0 (95)	0.082	Yes				
Benzo(a)pyrene	525.2	R2.0 (95)	0.16	No, 3 x MDL=0.48	0.1	0.2	0.004	0
	550	(7/90)	0.029	Yes				
	550.1	(7/90)	0.016	Yes				
Chlordane, Total	505	R2.1 (95)	0.14	No, 3 x MDL=0.42	0.1	0.1	0.03	0
	508	R3.1 (95)	--	--				
	508.1	R2.0 (95)	--	--				
	525.2	R2.0 (95)	--	--				
1,2-Dibromochloropropane (DBCP)	504.1	R1.1 (95)	0.01	No, 3 x MDL=0.03	0.01	0.2	0.0017	0
	551.1	R1.0 (95)	0.009	No, 3 x MDL=0.027				
Di(2-ethylhexyl)adipate	506	R1.1 (95)	12	No, 3 x MDL=36	5	400	none	400
	525.2	R2.0 (95)	1.3	Yes				
Di(2-ethylhexyl)phthalate	506	R1.1 (95)	2.2	No, 3 x MDL=6.6	3	4	12	0
	525.2	R2.0 (95)	0.46	Yes				
Dinoseb	515.1	R4.0 (89)	0.33	Yes	2	7	14	7
	515.2	R1.1 (95)	0.28	Yes				
	515.3	R1.0 (96)	0.82	No, 3 x MDL=2.46				
	555	R1.0 (92)	0.26	Yes				
Endrin	505	R2.1 (95)	0.063	No, 3 x MDL=0.189	0.1	2	1.8	2
	508	R3.1 (95)	0.006	Yes				
	508.1	R2.0 (95)	0.007	Yes				
	525.2	R2.0 (95)	0.16	No, 3 x MDL=0.48				
	551.1	R1.0 (95)	0.002	Yes				
Ethylene Dibromide (EDB)	504.1	R1.1 (95)	0.01	No, 3 x MDL=0.03	0.02	0.05	none	0
	551.1	R1.0 (95)	0.008	No, 3 x MDL=0.024				
Heptachlor	505	R2.1 (95)	0.003	Yes	0.01	0.01	0.008	0
	508	R3.1 (95)	0.002	Yes				
	508.1	R2.0 (95)	0.005	No, 3 x MDL=0.015				
	525.2	R2.0 (95)	0.059	No, 3 x MDL=0.177				
	551.1	R1.0 (95)	0.081	No, 3 x MDL=0.243				
Heptachlor Epoxide	505	R2.1 (95)	0.004	No, 3 x MDL=0.012	0.01	0.01	0.006	0
	508	R3.1 (95)	0.0059	No, 3 x MDL=0.0177				
	508.1	R2.0 (95)	0.001	Yes				
	525.2	R2.0 (95)	0.048	No, 3 x MDL=0.144				
	551.1	R1.0 (95)	0.002	Yes				

Pentachlorophenol	515.1	R4.0 (89)	0.032	Yes	0.2	1	0.4	0.0
	515.2	R1.1 (95)	0.16	No, 3 x MDL=0.48				
	515.3	R1.0 (96)	0.085	No, 3 x MDL=0.255				
	525.2	R2.0 (95)	1.0	No, 3 x MDL=3				
	555	R1.0 (92)	0.15	No, 3 x MDL=0.45				
	D5317-93	Vol. 11.02 ('99 thru '94)	0.076	No, 3 x MDL=0.228				
Picloram	515.1	R4.0 (89)	0.15	Yes	1	500	500	500
	515.2	R1.1 (95)	0.35	No, 3 x MDL=1.05				
	515.3	R1.0 (96)	1.0	No, 3 x MDL=3				
	555	R1.0 (92)	0.5	No, 3 x MDL=1.5				
	D5317-93	Vol. 11.02 ('99 thru '94)	0.14	Yes				
PCBs as Decachlorobiphenyl:	508A	R1.0 (89)			0.5	0.5	none	0
Aroclor 1221 as DCP			0.14	Yes				
Aroclor 1232 as DCP			0.23	No, 3 x MDL=0.69				
Aroclor 1242 as DCP			0.21	No, 3 x MDL=0.63				
Aroclor 1248 as DCP			0.15	Yes				
Aroclor 1254 as DCP			0.14	Yes				
Aroclor 1260 as DCP			0.14	Yes				
Simazine	505	R2.1 (95)	6.8	No, 3 x MDL=20.4	1	4	4	4
	507	R2.1 (95)	0.014	Yes				
	508.1	R2.0 (95)	0.008	Yes				
	525.2	R2.0 (95)	0.045	Yes				
	551.1	R1.0 (95)	0.142	Yes				
2,3,7,8-TCDD (Dioxin)	1613	Rev B 10/94)	4.4E-06	No, 3 x MDL=1.32E-5	5E-06	3E-05	none	0
Toxaphene	505	R2.1 (95)	1.0	No, 3 x MDL=3	1	3	none	0
	508	R3.1 (95)	--	--				
	508.1	R2.0 (95)	0.13	Yes				
	525.2	R2.0 (95)	1.0	No, 3 x MDL=3				
2,4,5-TP (Silvex)	515.1	R4.0 (89)	0.21	Yes	1	50	none	50
	515.2	R1.1 (95)	0.06	Yes				
	515.3	R1.0 (96)	0.14	Yes				
	555	R1.0 (92)	0.37	No, 3 x MDL=1.11				
	D5317-93	Vol. 11.02 ('99 thru '94)	0.075	Yes				